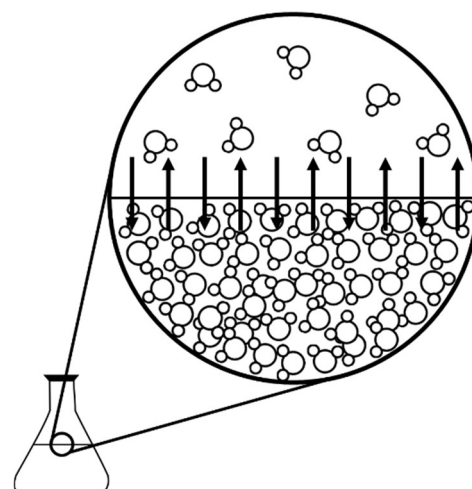**7.1 Introduction to Equilibrium**

Essential knowledge statements from the AP Chemistry CED:
- Many observable processes are reversible. Examples include evaporation and condensation of water, absorption and desorption of a gas, or dissolution and precipitation of a salt. Some important reversible chemical processes include the transfer of protons in acid-base reactions and the transfer of electrons in redox reactions.
- When equilibrium is reached, no observable changes occur in the system. Reactants and products are simultaneously present, and the concentrations or partial pressures of all species remain constant.
- The equilibrium state is dynamic. The forward and reverse processes continue to occur at equal rates, resulting in no net observable change.
- Graphs of concentration, partial pressure, or rate of reaction versus time for simple chemical reactions can be used to understand the establishment of chemical equilibrium.
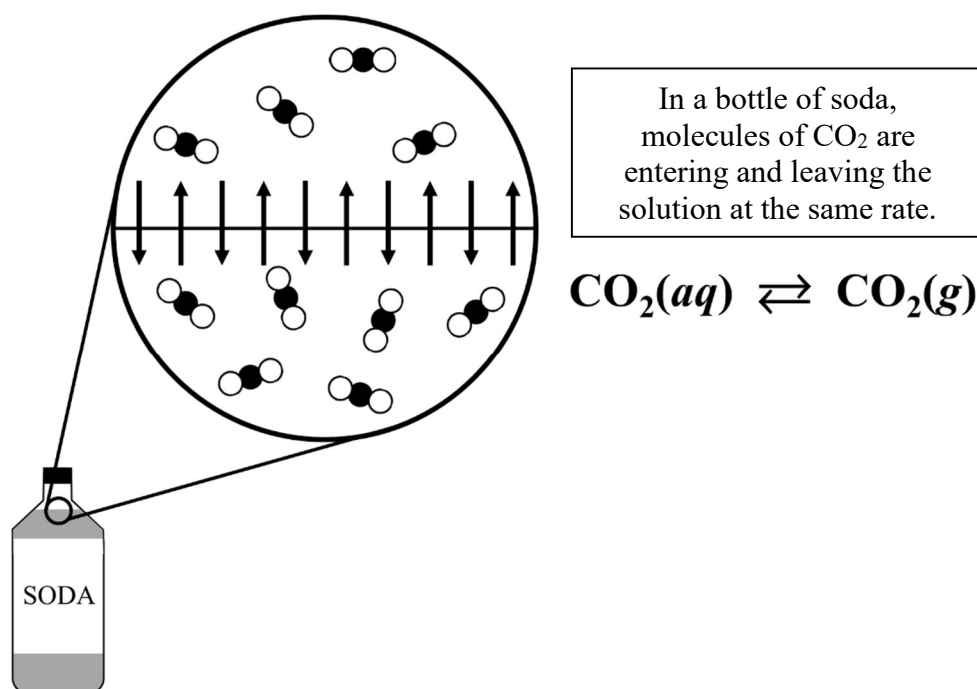

The diagram at right represents a sample of water in a sealed flask at constant temperature. The arrows in the close-up view show that water molecules undergo two opposing processes: evaporation and condensation. This can be represented by the following equation.
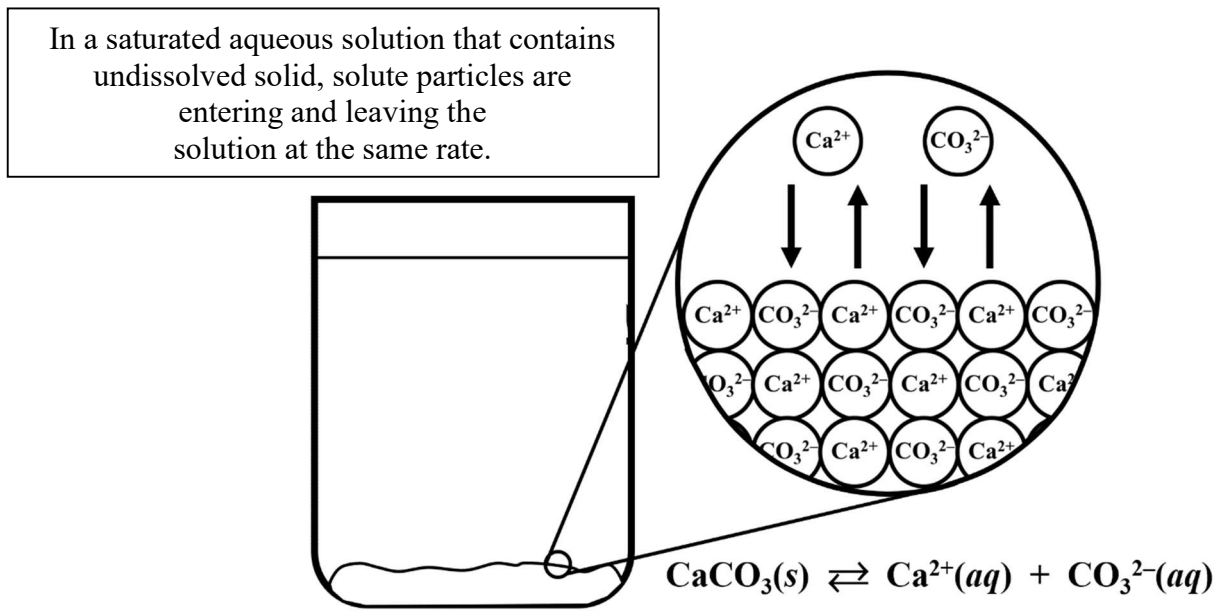
$$H_2O(l) \ \rightleftarrows \ H_2O(g)$$
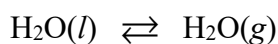
The double arrows ($\rightleftarrows$) in the equation above indicate that the *forward* process (evaporation) occurs from left to right, and the *reverse* process (condensation) occurs from right to left. At equilibrium, these opposing processes occur at the same rate.

Another example of equilibrium occurs in a solution of $CO_2(aq)$, as shown below.

In a bottle of soda, molecules of CO_2 are entering and leaving the solution at the same rate.

$$CO_2(aq) \rightleftarrows CO_2(g)$$

SODA

Another example of equilibrium occurs in a saturated aqueous solution that contains undissolved solid, as shown below.

In a saturated aqueous solution that contains undissolved solid, solute particles are entering and leaving the solution at the same rate.

$$CaCO_3(s) \rightleftarrows Ca^{2+}(aq) + CO_3^{2-}(aq)$$

Many chemical reactions can achieve a state of dynamic equilibrium, in which the *forward* reaction (from left to right) occurs at the same rate as the *reverse* reaction (from right to left).

1. Consider the decomposition of the substance $A_2X_4(g)$, which occurs according to the following equation.

$$A_2X_4(g) \rightleftarrows 2\ AX_2(g)$$
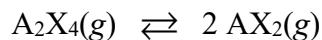
A sample of $A_2X_4(g)$ is added to a previously evacuated rigid reaction vessel. The partial pressures of each gas are monitored over time, and the data are shown on the graph below.
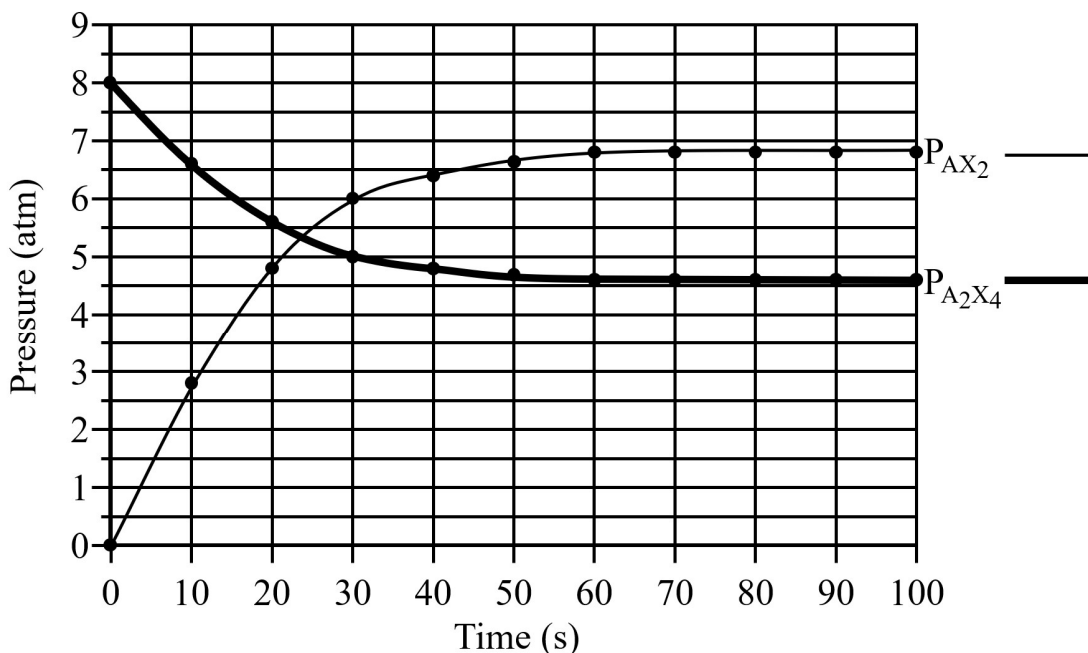
1. (continued)

(a) Use the information from the graph on the previous page to fill in the missing information in the data table below.
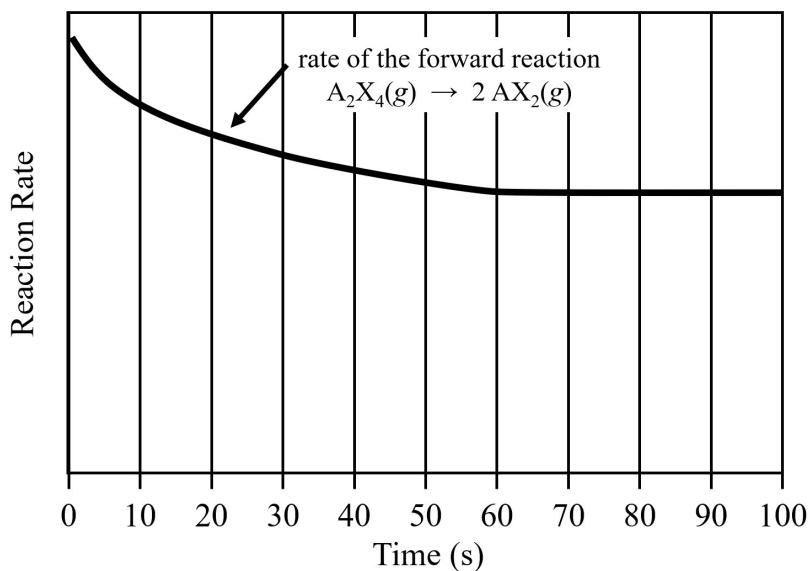
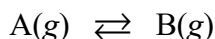| Time (s)	0	10	20	30	40	50	60	70	80	90	100
$P_{A_2X_4}$ (atm)			5.6			4.7					4.6
P_{AX_2} (atm)		2.8			6.4				6.8		

(b) At what point in time during the experiment did the reaction reach a state of equilibrium? Justify your answer.

(c) During the first 30 seconds of this experiment,

- the partial pressure of $A_2X_4(g)$ is (decreasing   increasing   )
- the rate of the *forward* reaction ($A_2X_4(g) \rightarrow 2\ AX_2(g)$) is (decreasing   increasing   )
- the partial pressure of $AX_2(g)$ is (decreasing   increasing   )
- the rate of the *reverse* reaction ($2\ AX_2(g) \rightarrow A_2X_4(g)$) is (decreasing   increasing   )

(d) A plot of the **reaction rate** for the *forward* reaction ($A_2X_4(g) \rightarrow 2\ AX_2(g)$) versus time is shown on the graph below. Draw a curve on the graph to show how the rate of the *reverse* reaction ($2\ AX_2(g) \rightarrow A_2X_4(g)$) changes over time.

rate of the forward reaction
$A_2X_4(g) \rightarrow 2\ AX_2(g)$

Reaction Rate

0   10   20   30   40   50   60   70   80   90   100
Time (s)

$$A(g) \;\rightleftarrows\; B(g)$$

2. Consider the system involving a reversible chemical reaction as described by the equation above. Decide if each of the following statements regarding equilibrium are true or false.

_____ If the rate of the *forward* reaction is greater than the rate of the *reverse* reaction, then equilibrium has not yet been achieved in this system.

_____ When equilibrium has been achieved in this system, the partial pressure of $A(g)$ should be equal to the partial pressure of $B(g)$.

_____ When equilibrium has been achieved in this system, the partial pressures of $A(g)$ and $B(g)$ should not change over time.

_____ When equilibrium has been achieved in this system, the particles of A and B should no longer collide or react with each other.

_____ When equilibrium has been achieved in this system, no observable changes will be detected, giving the appearance that nothing is happening in the reaction vessel.

7.2 Direction of Reversible Reactions

Essential knowledge statements from the AP Chemistry CED:
- If the rate of the *forward* reaction is greater than the rate of the *reverse* reaction, then there is a net conversion of reactants to products.
- If the rate of the *reverse* reaction is greater than that of the *forward* reaction, then there is a net conversion of products to reactants.
- An equilibrium state is reached when these rates are equal.

$$H_2(g) \;+\; I_2(g) \;\rightleftarrows\; 2\,HI(g)$$
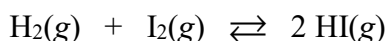
3. Consider the reaction between $H_2(g)$ and $I_2(g)$ to form $HI(g)$, as represented by the equation shown above. Different experiments were performed and were carried out at the same initial temperature.

Time 1			Time 2		
$[H_2]$	$[I_2]$	$[HI]$	$[H_2]$	$[I_2]$	$[HI]$
2.0 M	3.0 M	1.0 M	1.0 M	2.0 M	3.0 M

(a) Based on the information in the table above, which of the following is true about this system between Time 1 and Time 2?

_____ The rate of the forward reaction is greater than the rate of the reverse reaction.

_____ The rate of the reverse reaction is greater than the rate of the forward reaction.

3. (continued)

$$H_2(g) \ + \ I_2(g) \ \rightleftarrows \ 2\,HI(g)$$
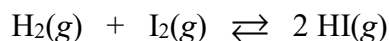
	Time 1			Time 2	
[H$_2$]	[I$_2$]	[HI]	[H$_2$]	[I$_2$]	[HI]
0.10 M	0.20 M	9.5 M	1.0 M	1.1 M	7.7 M

(b) Based on the information in the table above, which of the following is true about this system between Time 1 and Time 2?

_____ The rate of the forward reaction is greater than the rate of the reverse reaction.

_____ The rate of the reverse reaction is greater than the rate of the forward reaction.

7.3 Reaction Quotient and Equilibrium Constant

Essential knowledge statements from the AP Chemistry CED:
- The reaction quotient Q_c describes the relative concentrations of the reaction species at any time. For gas phase reactions, the reaction quotient may instead be written in terms of pressures as Q_p. The reaction quotient tends toward the equilibrium constant such that at equilibrium $K_c = Q_c$ and $K_p = Q_p$
- As examples, for the reaction $\ a\,A \ + \ b\,B \rightleftarrows c\,C \ + \ d\,D$

  o the equilibrium expression for K_c (or Q_c) is written as follows $\quad K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

  o the equilibrium expression for K_p (or Q_p) is written as follows $\quad K_p = \dfrac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$

- The reaction quotient does not include substances whose concentrations (or partial pressures) are independent of the amount, such as for solids and pure liquids.

$$a\,A \ + \ b\,B \rightleftarrows c\,C \ + \ d\,D$$
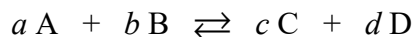
a, b, etc. = coefficients in the chemical equation

[A] = concentration of substance A (in units of mol/L) P_A = partial pressure of A (in units of atm)

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$ $$Q_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

The subscript "c" indicates that concentration values (mol/L) are used in the expression.   The subscript "p" indicates that pressure values (atm) are used in the expression.

The difference between the **reaction quotient Q** and the **equilibrium constant expression K** is outlined in the table below. *The value of Q is equal to K when the system is at equilibrium.*

| Reaction Quotient (Q) Evaluated at any point during the reaction	Equilibrium Constant Expression (K) Evaluated when the system is at equilibrium
$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{or} \quad Q_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$	$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{or} \quad K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$
You solve for Q by substituting in the values for the concentrations (or partial pressures) of the reactants and the products *at any point during the reaction.*	You solve for K by substituting in the values for the concentrations (or partial pressures) of the reactants and the products *when the system is at equilibrium.*

4. For each of the following chemical equations, write the equilibrium constant expression for both K_c and K_p. **Note that solids and pure liquids are not included in the reaction quotient Q or in the equilibrium constant expression K.**

Chemical Equation	K_c	K_p
$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$		
$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$		
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$		
$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq)$		not applicable because no gases are present
$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$		not applicable because no gases are present

7.4 Calculating the Equilibrium Constant

Essential knowledge statement from the AP Chemistry CED:
- Equilibrium constants can be determined from experimental measurements of the concentrations or partial pressures of the reactants and products at equilibrium.

$$N_2O_4(g) \;\rightleftharpoons\; 2\,NO_2(g)$$
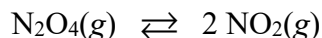
5. A series of experiments was performed in the laboratory based on the reaction represented above. Each reaction was carried out at a temperature of 373 K.

   (a) Calculate the change in concentration for each substance in each experiment.

Expt. 1	$[N_2O_4]$ (M)	$[NO_2]$ (M)
Initial	10.00	0.00
Change		
Equilibrium	9.30	1.40

Expt. 4	$[N_2O_4]$ (M)	$[NO_2]$ (M)
Initial	3.00	6.00
Change		
Equilibrium	5.46	1.08

Expt. 2	$[N_2O_4]$ (M)	$[NO_2]$ (M)
Initial	0.00	10.00
Change		
Equilibrium	4.51	0.98

Expt. 5	$[N_2O_4]$ (M)	$[NO_2]$ (M)
Initial	8.00	1.00
Change		
Equilibrium	7.86	1.28

Expt. 3	$[N_2O_4]$ (M)	$[NO_2]$ (M)
Initial	10.00	10.00
Change		
Equilibrium	14.14	1.72

Expt. 6	$[N_2O_4]$ (M)	$[NO_2]$ (M)
Initial	2.00	3.00
Change		
Equilibrium	3.10	0.80

   (b) The value for $\left| \dfrac{\text{change in } [NO_2]}{\text{change in } [N_2O_4]} \right|$ in all six experiments is equal to _____

   which is consistent with the coefficients from the chemical equation.

5. (continued)

(c) The equilibrium concentrations from Experiments 1-6 are shown below. Calculate the value of the equilibrium constant K_c for each experiment (at 373 K). Round off your answers to two significant figures.

Expt.	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K_c = \dfrac{[NO_2]^2}{[N_2O_4]}$
1	9.30	1.40	
2	4.51	0.98	
3	14.14	1.72	
4	5.46	1.08	
5	7.86	1.28	
6	3.10	0.80	

The value of the equilibrium constant K is normally calculated at a specific temperature. If you change the temperature at which the reaction is carried out, the value of K should also change.

_____

$$H_2(g) \;+\; I_2(g) \;\rightleftarrows\; 2\,HI(g)$$
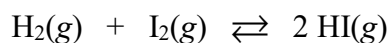
6. The system represented by the equation above reached equilibrium at 448°C. The concentrations of the substances in the reaction vessel at equilibrium were determined to be the following.

$$[H_2] = 0.80\ M \qquad [I_2] = 0.54\ M \qquad [HI] = 4.7\ M$$

(a) Calculate the value of the equilibrium constant (K_c) for this system at 448°C. Round off your answer to two significant figures.

(b) In a separate experiment, samples of $H_2(g)$ and $I_2(g)$ were added to a previously evacuated reaction vessel, with an initial concentration of 0.25 M for each substance. The reaction was allowed to proceed at 448°C until the system reached equilibrium. Should the concentration of $H_2(g)$ in the reaction vessel at equilibrium be less than or greater than 0.25 M? Justify your answer.

6. (continued)

$$H_2(g) \ + \ I_2(g) \ \rightleftarrows \ 2\,HI(g)$$
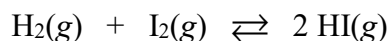
Another experiment was performed with this system. At a certain point in time, the concentrations of the substances in the reaction vessel at 448°C were determined to be the following.

$$[H_2] = 0.15 \ M \qquad [I_2] = 0.25 \ M \qquad [HI] = 3.2 \ M$$

(c) With the concentrations listed above, is this system at equilibrium? Justify your answer by calculating the value of the reaction quotient (Q_c) for this system at 448°C.

(d) In which direction, toward the left (reactants) or toward the right (products), should the reaction proceed in order to achieve equilibrium? Justify your answer.

Suppose that you already know the value of the equilibrium constant (K) for a certain reaction at a certain temperature, and you also know the values for the concentrations (or partial pressures) of the reactants and the products at a certain point in time. You calculate the value of the reaction quotient (Q).

When you compare Q with K, you can determine which one of the following situations is true.

- Q is equal to K. The system has already reached equilibrium.

- Q is less than K. There are "too many reactants" or "not enough products." A net conversion of reactants to products, from left to right, occurs until equilibrium is achieved and $Q = K$.

- Q is greater than K. There are "too many products" or "not enough reactants." A net conversion of products to reactants, from right to left, occurs until equilibrium is achieved and $Q = K$.

Mnemonic Devices to Help You Remember the Consequences of Q vs. K

Q vs. K	Too Many or Not Enough	Inequality Symbol Used as an Arrow (K written before Q)	Consequence
Q is less than K	$\dfrac{\text{products}}{\text{reactants}}$	$K > Q$	net conversion of reactants to products from left to right until equilibrium is achieved
Q is greater than K	$\dfrac{\text{products}}{\text{reactants}}$	$K < Q$	net conversion of products to reactants from right to left until equilibrium is achieved

$$H_2(g) \; + \; I_2(g) \; \rightleftarrows \; 2\,HI(g) \qquad K_c = 51 \text{ at } 448°C$$

7. For each set of experimental conditions listed in the table below,
   - Use the data to calculate the value of the reaction quotient (Q_c).
   - Compare K_c with Q_c and choose one of the following consequences.
     - The system is already at equilibrium.
     - The system should proceed toward the products (from left to right) until equilibrium is achieved.
     - The system should proceed toward the reactants (from right to left) until equilibrium is achieved.

	$[H_2]$	$[I_2]$	$[HI]$	Q_c	K_c vs. Q_c ?	Consequence
#1	0.35 M	0.45 M	3.0 M			
#2	1.6 M	1.4 M	4.2 M			
#3	0.90 M	0.81 M	6.1 M			

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

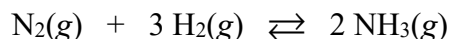8. Consider the system represented by the equation above. A sample of pure $COCl_2(g)$ is added to a previously evacuated rigid reaction vessel at 690 K. The initial pressure in the reaction vessel (before any reaction occurs) is 1.0 atm. After the system has reached equilibrium at 690 K, the total pressure in the reaction vessel is 1.2 atm.

    (a) Determine the partial pressure of each substance in the reaction vessel at equilibrium.

    (b) Calculate the value of K_p for the reaction at 690 K.

One of the reasons that makes Question #8 a challenging problem is that it seems like you don't have enough information to calculate the value of K_p. This question is easier to solve if you create a R-I-C-E table.

R eaction	$COCl_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$Cl_2(g)$
I nitial					
C hange					
E quilibrium					

When you are filling in the information in the "Change" row of the R-I-C-E table, the change in the amount of each substance (in concentration or in pressure) should be proportional to the coefficients in the balanced equation.

$$N_2(g) \ + \ 3\,H_2(g) \ \rightleftharpoons \ 2\,NH_3(g)$$

9. Consider the system represented by the equation above. Samples of all three substances were added to a previously evacuated rigid reaction vessel at 300 K. The initial values for the partial pressures of the substances in the reaction vessel were determined to be the following.

$$P_{N_2} = 6.7 \text{ atm} \qquad P_{H_2} = 6.0 \text{ atm} \qquad P_{NH_3} = 0.2 \text{ atm}$$

After the system has reached equilibrium at 300 K, the partial pressure of $NH_3(g)$ is 1.4 atm.

(a) Determine the partial pressure of each substance in the reaction vessel at equilibrium.

(b) Calculate the value of K_p for the reaction at 300 K.

Hint: Create a R-I-C-E table to solve this problem.

7.5 Magnitude of the Equilibrium Constant

Essential knowledge statement from the AP Chemistry CED:
- Some equilibrium reactions have very large K values and proceed essentially to completion. Others have very small K values and barely proceed at all.

$$2\,NO(g) \ + \ O_2(g) \ \rightleftharpoons \ 2\,NO_2(g) \qquad K_p = 6.4 \times 10^9$$

10. When the reaction represented by the equation above reaches equilibrium, which of the following substances should have a higher value for partial pressure in the reaction vessel? Circle your choice, and justify your answer.

$$NO(g) \qquad\qquad NO_2(g)$$

$$HCN(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + CN^-(aq) \qquad K_c = 6.2 \times 10^{-10}$$
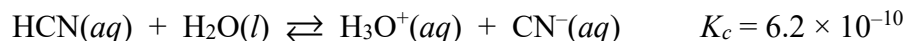
11. When the reaction represented by the equation above reaches equilibrium, which of the following substances should have a higher concentration? Circle your choice, and justify your answer.

    $HCN(aq)$ $CN^-(aq)$

12. (a) When the value of K is very small, the (reactants   products) are favored at equilibrium.

    (b) When the value of K is very large, the (reactants   products) are favored at equilibrium.

$$CH_4(g) + 2\,H_2S(g) \rightleftarrows CS_2(g) + 4\,H_2(g) \qquad K_c = 3.3 \times 10^4 \text{ at 1200 K}$$

13. Samples of $CH_4(g)$ and $H_2S(g)$ are introduced into a previously evacuated rigid container. The initial concentrations of these substances are the following.

$$[CH_4] = 0.30\ M \qquad\qquad [H_2S] = 1.0\ M$$

The temperature is held constant as the reaction represented by the equation above reaches equilibrium at 1200 K.

(a) Considering the value of K_c, calculate the final concentration of $H_2S(g)$, $CS_2(g)$, and $H_2(g)$ in the reaction vessel after the system reaches equilibrium at 1200 K.

(b) The final concentration of $CH_4(g)$ in the reaction vessel at equilibrium is very small, but not exactly zero. Calculate the concentration of $CH_4(g)$ at equilibrium.